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O VLIYANII MAKROOBRASTANIYA NA KCRROZIYU STALEY V CHERNOM MORE

(The Effect of Macrofouling on Steel Corrosion in the Black Sea)

by

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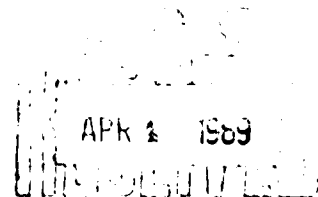WASHINGTON 25, D. C.

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ABSTRACT

In order to investigate the effect of organic fouling, notably barnacles, on steel in the Black Sea, special tests have been conducted with the aid of marble and steel plates. The plates have been covered by barnacles and kept in laboratory conditions, as well as in the sea, for various time periods. As a result, it is established that the products of metabolism and reproduction of marine foulers do not further the development of steel corrosion. Only in cases when barnacles are loosely attached to the metal is the process of corrosion observed, which, according to special tests, is caused by electrochemical processes.

The Translator

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THE EFFECT OF MACROFOULING ON STEEL CORROSION IN THE BLACK SEA

In connection with urgent practical requirements, the problem of metal
corrosion in the sea is, with each year, attracting more attention by
investigators. In the general literature, that has accumulated so far
relative to the problem, the role of the biological factor in the cor-
rosion process has been repeatedly mentioned (Bengough, Shepheard,
1943; Negreyev and Kyazimov, 1958; Petrakki, 1959; Transactions of the
All-Union Conference on the Struggle with Sea Corrosion, 1958; Ulanov-
skiy, Tarasov and Korovin, 1959). However, the effect of organic foul-
ing, notably macrofouling, on the corrosion of metals in the sea has
not yet been elucidated in its substance.

This paper lists some of the data of investigations dealing with the
effect of organisms of macrofouling on the corrosion of steel in the
Black Sea. The main object of the study was the barnacle (Balanus
improvisus Darwin) as a most widely distributed fouler (Nikitin, 1947).

At the beginning of the investigation, we verified the suggestion ex-
pressed by several authors (Akimov, 1946) relative to the possible ef-
fect of the products of barnacle metabolism on steel corrosion. For
this purpose, such chemical characteristics of the liquid of the pal-
lial cavity as the content of chlorine ions, the pH value and the
oxygen quantity were determined.

Table 1

A COMPARATIVE CONTENT OF CHLORINE IONS (G/KG) IN THE
LIQUID OF THE PALLIAL CAVITY OF BARNACLES AND IN SEA WATER

No. of test	Liquid of pallial cavity	Sea water	No. of test	Liquid of pallial cavity	Sea water
1	9.22	9.97	5	9.27	9.92
2	9.13	9.89	6	9.03	10.04
3	9.27	9.89	Mean	9.19	9.95
4	9.22	9.97			

Remark. Altogether, 60 animals were investigated in the tests.

These studies were carried out at the Black Sea Scientific Investigational Station of the Institute of Oceanology of the Academy of Sciences of the USSR in Gelendzhik jointly with I. B. Ulanovskiy and Yu. M. Korovin.

The quantity of chlorine ions was determined by the micromethod of Bruyeovich (1933). The chlorine content in sea water was used here for /267 control purposes. The results of the tests are listed in Table 1.

It is seen from the table that the quantity of chlorine ions in sea water exceeds the quantity of the ion in the liquid of the pallial cavity of barnacles. Assuming that the quantity of chlorine in sea water is 100 %, in the pallial cavity of barnacles the quantity of chlorine will be 92.4 %. Because the corrosion of steel intensifies with increase in the concentration of chlorine ions (Akimov, 1952), and the experiments demonstrate that their quantity in the liquid of the pallial cavity is smaller than in the sea, this excludes the possibility of an increased corrosive action on metals of the liquid found in the pallial cavity of barnacles.

The determination of the pH value, which exercises a substantial influence on the process of steel corrosion (Akimov, 1952), was made in the liquid of the pallial cavity of barnacles by the potentiometric method with the use of a quinhydrone electrode, and with the aid of a universal indicator known as ZIV-1. The pH value was measured in:
a) the dome of the barnacles maintaining a constant interchange with the surrounding water (in the case of the so-called open barnacles);
b) the barnacles kept two hours in the air prior to the test; part of the barnacles had been isolated by means of paraffin from the surrounding medium; c) the water layer adjacent to the domes of the barnacles. The pH value in sea water was in all instances used for control purposes. The results of measurements of pH values in the pallial cavity of barnacles are listed in Table 2.

It is seen from Table 2 that the pH value of sea water is greater than the pH value of the liquid found in the pallial cavity of barnacles, which is explained by the liberation of acid products in the pallial cavity. This difference increased with exposing the barnacles to the air. Still greater is the reduction of the pH value in the pallial liquid of the barnacles that have been isolated from the surrounding medium by means of paraffin (as a result of a complete absence of oxygen, the products of metabolism accumulate in the dome). However, even in this case the mean pH value is smaller than that of sea water, the difference being 6 per cent. As is known from the literature (Akimov, 1946), such a reduction in the pH value cannot but exercise a substantial effect on the electrode potential and, consequently, also on the corrosion resistance of steel. The pH values determined in various

locations of containers filled with sea water, where groups of barn-
acles had been kept for a day, disclose the following: the pH value
found in water that is contiguous to the domes of barnacles does not
change as the water flows away, which is explained by the natural inter-
mixing of waters (in the consequence of heat diffusion and the motion
of the cirri of barnacles). This points out that the end products of
metabolism, that are liberated through the roofs of the domes, are
intermixing with sea water and dispersing throughout the containers
without practically decreasing the pH value in the layer that is contig-
uous to the barnacles. In the sea, where a constant and intense inter-
mixing exists, the presence of a special water layer around the barn-
acle organisms,[1] in which the pH value could differ considerably from
that of the environment, is still less probable. This was accomplished
by direct observations on a sunken barge in the sea, where the pH
value was measured in the organic fouling consisting of barnacles
(Table 3).

Table 2

THE RELATIVE VALUE OF pH (ON THE BASIS OF SELECTED DATA)
IN THE LIQUID OF THE PALLIAL CAVITY OF BARNACLES AND IN THE SEA WATER

Number of tests	Liquid of the pallial cavity of barnacles (diameter not less than 10 mm)			Sea water
	without exposing to the air	exposed to air for two hours	protected by paraffin for two hours	
1	7.68	7.46	7.30	7.84
2	7.66	7.47	7.38	7.80
3	7.63	7.44	7.35	7.80
4	7.61	7.56	7.45	7.87
5	7.63	7.52	7.40	7.82
Mean	7.64	7.49	7.37	7.82

[1] It need be noted that in the case of organic fouling consisting of
barnacles, mollusks, bryozoans, hydroids, and golden-stars the inter-
mixing of water will not, evidently, be complete and the waste products
of such a biocoenose may accumulate in the layer that is contiguous to
metal, thus affecting its corrosion.

Table 3

Number of measurement	pH in sea water	
	among barnacles	far from barnacles
1	8.3	8.16
2	8.11	8.4
3	7.94	8.2
4	8.2	8.03
Mean	8.14	8.19

In order to determine the quantity of oxygen in the liquid of the pallial cavity of barnacles, it was necessary to find the differences between this magnitude and the quantity of oxygen in sea water. It is known that the speed of corrosion increases at a small quantity of oxygen and with a simultaneous reduction in the pH value (Akimov, 1945; 1951). Consequently, a reduction in the quantity of oxygen in the liquid of the pallial cavity of barnacles (especially when the domes are tightly covered) may play a significant role in the process of metal corrosion.

The work was done with large specimens of barnacles. The oxygen quantity in water was determined by the method of closed containers (the Winkler method), whereas its quantity in the pallial liquid was determined by the Krogh micromethod. Three series of tests were carried out in order to determine the oxygen content: a) in sea water taken by a syringe from the layer contiguous to the shell of barnacles and from a layer lying at a certain distance from them; b) in the liquid of the pallial cavity of "open" barnacles (15 to 20 specimens in each test), and c) in the liquid of the pallial cavity of "closed" barnacles (also 15 to 20 specimens in each test). The oxygen content in running sea water of the container was used as a control value.

As a result of the tests, we found, first of all that there was no difference between the oxygen quantity in the control container and the water samples taken from the layer contiguous to the shell of the barnacles. This indicates once more (as in the case of pH value) that, if there is no difference in the quantity of oxygen in the water of the container (the volume being 0.5 l) lying around the barnacles and

farther from them, it is impossible to assume the existence of differences in natural conditions where the water movement is uninterrupted. The observations carried out in the sea confirmed the situation (Tables 4 and 5).

Table 4

OXYGEN QUANTITY IN THE WATER OF THE CONTAINER (ML/G)

No. of test	At a distance from the barnacles	By the shell of the barnacles
1	10.052	10.050
2	10.390	10.396
3	10.510	10.505
4	10.382	10.382
Mean	10.333	10.333

Table 5

OXYGEN QUANTITY IN THE SEA

No. of test	At a distance from the barnacles	By the shell of the barnacles
1	9.766	9.770
2	9.704	9.712
3	9.790	9.790
Mean	9.753	9.757

The tests aimed at determining the oxygen quantity in the pallial cavity of the barnacles ("open" and "closed" barnacles) demonstrated that, despite the attempt to modify the taking of samples with the aid of a

syringe, the Krogh method was unacceptable for the determination of oxygen in a liquid taken from various barnacles because great discrep-ancies resulted from it.

Evidently, such variations need to be measured by the polarigraphic or the capillary calorimetric methods of oxygen determination. But since it was technically impossible for us to apply these methods, we decided that an indirect way by using our previous data (Arbuzova, 1957) was expedient for the calculation of oxygen consumption in the pallial cav-ity of barnacles.

The calculation disclosed that in the dome of "open" barnacles, in which a constant exchange with the surrounding medium takes place, the oxygen quantity differs very little (5 %) from that in sea water.

In the Black Sea where the salinity is 18 %/oo, the barnacles are able to close their dome for five minutes to one hour, but in water with re-duced salinity the dome can be closed for 10 hours (Arbuzova, 1957). With such a lengthy and tight closing of the dome, the oxygen contained in it must, evidently, be completely exhausted. Assuming that barna-cles, when closing their domes, utilize the oxygen with the usual speed, all the oxygen contained in the pallial cavity will, according to our calculations, be consumed in 14 seconds. But since the use of oxygen by barnacles decreases with its reduction (Moore, 1935), the time needed for a complete consumption of oxygen will, undoubtedly, be longer. In this case the reduction in the quantity of oxygen in the domes of barnacles could lead to a loss of protective properties in the steel surface. However, when opening the dome, the liquid of the pallial cavity of barnacles rapidly intermixes with the surrounding wa-ter, thus becoming enriched with oxygen.

Thus, the explanation of a change in the chemical composition of water in the layer contiguous to the metal by fouling (mainly by barnacles), that has been formed in one warm season in the Black Sea, seems to be unconvincing. It is more probable that the chemical effect of pro-ducts resulting from the metabolism of barnacles on the corrosion of metal, provided there is such an effect, can be induced only by their reaching the metal through the base of the dome. We did not find any data in literature that would pertain to the problem of penetrability in the base of the domes of barnacles. Therefore, the subsequent in-vestigation of the effect of fouling, caused by barnacles on the cor-rosion of metal in the Black Sea, was devoted to the determination of penetrability of calcareous bases of domes of barnacles. The results of the investigation are discussed in this paper (Arbuzova, 1959). The main conclusions can be summarized as follows.

1. The base of the domes of live barnacles is impenetrable for the Ca^{45} isotope dissolved in sea water and, evidently, for the products of metabolism. Therefore, even if corrosion is present under live barnacles, it cannot be considered as a consequence of the action of the products of metabolism on the metal.

2. As the barnacles with closed dome tops die (which is possible in natural conditions when bryozoans, sponges and other organisms settle on barnacles), the resultant products of their decomposition gradually dissolve the thin parts of the base of their domes within two or three weeks. The base becomes penetrable to radioactive solutions and to the products of barnacle decomposition which, coming in contact with metal, further its corrosion. The facts can be explained by the formation of a local corrosion (corrosion pit) formed under dead barnacles, which has been discussed by a number of authors (La Que and Clapp, "Marine fouling..." 1945, 1952). In the most frequently occurring cases, i.e. when barnacles are being decomposed with open dome tops, the remains of their bodies and the products of decomposition are washed away by water and, thus, the dissolution of the bases of domes does not take place.

However, the observations and special experiments carried out by us with a view to studying organic fouling and corrosion of steel plates in the sea and in the laboratory led to somewhat unexpected results.

The test plates of stainless steel of the 1X18H9T brand, of carbon steel St3, as well as of polished marble were submerged in the sea in 1958 and 1959 at the marine stand of the Batumi Corrosion Station IFKhAN.

In order to verify whether or not the dissolution of the bases of barnacle domes results from the products of their decomposition and to find the effect of the latter on the surface of metal, 10 barnacles were killed and covered by plasticine on each steel plate. The first group of the plates was taken out of the sea in two weeks, the other group in a month after the beginning of the test. In both of the cases, no dark spots or corrosion pits were observed under the bases of decomposing barnacles.

It can be thought that, even if a dissolution of the thin base of barnacles by the products of their decomposition had taken place during this time, also a neutralization of the products may have occurred, and, hence, the absence of corrosion under the barnacles. On the other hand, it is possible that, as a result of the direct effect of acid products of decomposing barnacles on the metal, a longer time for the appearance of visible corrosion marks was needed after the products had decomposed the calcareous base.

Similar results were obtained also from the third group of plates on
which the barnacles had been killed and covered by plasticine. The
plates were put into battery jars with irremovable sea water and ex-
posed to the sunlight in the area of the corrosion station. In a
month's time, during which all the animals had been decomposed, the
entire surface of the metal was darkened except for the part covered /271
by the domes of the barnacles. Only under three "open" barnacles,
which were alive at the beginning of the experiment, did we observe
dark spots. Obviously, the corrosion of metal beneath them had been
created by causes not associated with the effect of the organisms.

In order to specify the problem of the effect of corrosion products of
dead animals and of metabolic products of live barnacles, in 1959 we
carried out experiments on plates made of polished marble which could
be readily subjected to destruction and excluded the electrochemical
corrosion. An examination of the plates after six months of submer-
gence in the sea disclosed the absence of even a slight damage to the
polish, though the fouling was significant. This means that, if the
products of metabolism and decomposition did not affect the marble
plates during this time period, it is still less possible that they
would affect steel. The absence of marble corrosion under the barna-
cles emphasizes once more that the base of live, as well as of dead
barnacles are impenetrable (there were no decomposing barnacles with
closed tops of domes on the plates). The well-preserved surface of
marble in areas devoid of organic fouling indicates that the products
of metabolism and decomposition of barnacles do not affect the sur-
rounding substrate because they, evidently, lose their acid character.

Simultaneously, we carried out a series of tests with several small
plates of steel St3 and of stainless steel 1X18H9T, on which several
spots of paraffin and plasticine were put prior to their placement in
the sea. For two months, the plates placed in the sea as well as
those placed in weakly running water in the laboratory remained entire-
ly bright, i.e. without corrosion, under all of the paraffin and plas-
ticine spots. Evidently, this is explained by the fact that paraffin
and plasticine lie tightly on metal, as a result of which sea water
cannot penetrate the interface.

In order to prove it, we conducted supplementary observations on or-
ganic fouling and steel corrosion on plates made of carbon, and espe-
cially of stainless steel 1X18H9T on which the corrosion processes
characterized by the formation of deep corrosion pits occur most
rapidly and visibly.

The surface of eight plates of carbon steel St3 (the size being 180x
250 mm), which had been submerged in the sea for five months, was over-
grown with a layer of barnacles (B. improvisus and B. eburneus Gould)

and the bryozoan (Lepralia pallasiana Moll). Some tubes of Mercierella
enigmatica Fauvel were on the organisms. On the upper layer were found
well-developed colonial Botryllus, which had settled quite recently,
covering almost the entire surface of the plates. The corrosion on the
plates was rather pronounced. A layer of dense corrosion products
(ferric oxide of rusty color) covered the greater part of the plates,
so that many organisms had, evidently, attached themselves to this lay-
er; and they could be readily separated from the metal together with
the rust. No local corrosion centers were noticed on the surface of
metal underneath the animals. On the other hand, under the barnacles
(no matter whether they were alive or dead) lying on the surface of
metal, that was not covered by a thick layer of corrosion products, we
observed dark corrosion spots in a number of cases.

The plates of stainless steel (1X18H9T) had preserved a smooth surface,
which had only slightly darkened, for the entire period of submergence
(two and six months). Small patches of rust were observed only on some   /272
of the plates, around openings along their upper edge, through which
passed wires protected by a chlorine-vinyl jacket and used for fasten-
ing the stand to the frames. The marine fouling on the plates was a-
bout the same as on the plates of carbon steel. No traces of corrosion
were noticed after the removal of worm tubes and bryozoan colonies from
the plates.

At the same time we found under several single barnacles (live and dead,
of various sizes) corrosion pits in the form of horse shoes, cavities,
circles, and holes, which sometimes reached the depth of 1 to 2 mm in
the plates whose thickness was 3 mm. A statistical processing of the
material enabled us in 1959 to characterize the frequency of occurrence
of corrosion pits under barnacles. Out of 10,630 examined barnacles
the corrosion pits were observed only under 16 of them, which made up
only 0.15 % of their total number.

It is interesting to note that a special test with plates enclosed in
a frame, surrounded by planktonic gas, made it possible to observe the
corroding of stainless steel in the absence of organic fouling. Sev-
eral corrosion centers were observed on the plates, one of which had
the form of an opening. Their formation has to be explained by certain
internal defects in the metal that was corroding rapidly and intensely
under the influence of sea water.

Thus, on the basis of the above-mentioned experiments and observations
on organic fouling and corrosion, at least with respect to the plates
of stainless steel, it is possible to conclude that the cause of metal
corrosion under some of the barnacles may be their loose attachment to
the object. Possibly, cracks are formed under some of the barnacles
in the process of growth, which are penetrated by sea water, creating
conditions in which, due to retarded metabolism, a galvanic couple is

developed. Narrow gaps may serve as centers for the development of
bacteria which, in turn, further the formation of electrochemical cor-
rosion (Ulanovskiy, Rosenberg, and Korovin, 1959).

In order to prove the supposition, tests for the determination of the
presence of gaps under barnacles were conducted on glass plates in
1959 at Batumi by applying the method of the luminescent defectoscope
(Arbuzova and Patrikeyev, 1960).

The tests disclosed that in a few cases (0.3 %) narrow gaps existed
between the object and the base of barnacles. With the presence of
such gaps on steel plates, which was disclosed by nickelplating of the
latter, the development of electrochemical corrosion is possible.

As a result of special tests, it was established that the products of
metabolism and reproduction of marine foulers in the Black Sea do not,
as a rule, further the development of corrosion processes on metal to
which they are fastened. The steel corrosion is observed under barna-
cles (no matter whether they are alive or dead) that are loosely attach-
ed to its surface, and is the result of electrochemical processes.

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